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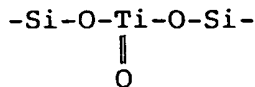
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(54) Catalyst and process for producing oxirane compound

(57) A heterogeneous catalyst used for producing an oxirane compound by reacting an olefinic compound with an organic hydroperoxide which catalyst is substantially insoluble in the reaction mixture, comprises at least one silicon compound, selected from the group consisting of silica and inorganic silicates, in chemical combination with an oxide or hydroxide of titanium, and is obtained by a process comprising the steps of

- (a) impregnating the silicon compound with a titanium compound in a solvent for impregnation,
- (b) removing the solvent for impregnation
- (c) then washing the remaining composition with a washing solvent and removing the washing solvent, and
- (d) then calcining the residual composition.

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The solid silica and/or inorganic silicates used in the present invention contain preferably at least 50%, more preferably at least 75%, most preferably at least 90%, in the form of its dioxide, of silicon. The solid silica and/or inorganic silicates preferably have a relatively large specific surface area. The specific surface area is preferably at least 1 m²/g, more preferably 25-800 m²/g.

The silica is preferably synthetic porous silica of a relatively high density and of close pack type which is composed of amorphous silica particles coagulated or bound to one another, and may be, for example, silica gel, precipitated silica, or the like. The method of preparation of such synthetic silica and its properties are described in "The Colloid Chemistry of Silica and Silicates", (written by R. G. Iler, pub. by Cornell University Press, New York, U.S.A., 1955, Chapter VI) and U.S.P. No. 2,657,149. Among the silica gels available on the market, those which have a specific surface area of 25-700 m²/g, pore volume of 0.3-2.0 ml/g and silica content of at least 99% by weight are preferably used. Silica powders consisting of particles of amorphous silica flocculated in open-packed, readily disintegrated, loosely knit aggregates may also be favorably used. An example of such silica is fumed pyrogenic silica obtained by subjecting hydrogen and oxygen together with silicon tetrachloride or silicon tetrafluoride to combustion operation. Various silicas of this kind are available on the market, which include, for example, Cab-o-sil (a registered trade mark, mfd. by Cabot Corporation) and Aerosil (a registered trade mark, mfd. by Degussa). Particularly preferred among these silica products are those which have a specific surface area of 50-500 m²/g and silica content of at least 99%.

Crystalline aluminosilicates known as molecular sieves may also be used as the solid silica and/or inorganic silicates. Naturally occurring crystalline silicates may also be used, examples of which include asbestos minerals, such as serpentine (hydrous magnesium silicate), clay minerals, such as hectorite (lithium magnesium silicate), kaolin and bentonite, and mica minerals, such as phlogopite (aluminum magnesium potassium silicate) and vermiculite (hydrous magnesium silicate).

Among these kinds of silica and silicates described above, synthetic amorphous solid silica and/or inorganic silicates are preferably used, and those which consist substantially of pure silica and have a silica content of, for example, at least 95% are particularly preferably used.

The solvents used for impregnation and washing may be oxygen containing organic solvents which have 1 to about 12 carbon atoms and are liquid at ordinary temperature. They are, for examples, alcohols, ketones, ethers (both acyclic and cyclic) and esters. Specific examples thereof include alcohols, such as methanol, ethanol, ethylene glycol, propylene glycol, isopropanol, n-butanol and octanol; ketones, such as acetone, diethyl ketone, methyl ethyl ketone and methyl isobutyl ketone; hydrocarbon ethers, such as diisobutyl ether and tetrahydrofuran, and hydrocarbon esters, such as methyl acetate, ethyl acetate, butyl acetate and butyl propionate.

Though the solvent for impregnation and the washing solvent may be the same or different, preferably used as the washing solvent are above-mentioned alcohols.

The titanium compounds used in the present invention may be soluble titanium salts of inorganic acids or organic acids and titanate acid esters. Specific examples of the titanium compounds include tetramethyl titanate, tetraethyl titanate, tetrapropyl titanate, tetraisopropyl titanate, tetrabutyl titanate, tetraisobutyl titanate, tetra-2-ethylhexyl titanate, tetraoctadecyl titanate, titanium tetrachloride, titanium tetrabromide, titanium tetraiodide, titanium (IV) oxyacetylacetonate, and titanium (IV) diisopropoxide bisacetylacetonate. When alcohols or ketones are used as the solvent for impregnation, titanium tetrachloride and lower titanate acid esters are preferably used.

The impregnation solution preferably has a titanium concentration of about 0.01 mol/l to about 1.0 mol/l. Specific examples of the solution include an alcohol solution of titanium tetrachloride and a solution of a titanate acid ester having 1-10 carbon atoms per alkoxy group in an alcohol having 1-10 carbon atoms. The concentration of the titanium compound in the impregnation solution and the amount of the solution used are preferably adjusted so as to give a titanium content in the ultimate catalyst in the range of about 0.1 to about 10% by weight, as calculated in terms of the titanium amount relative to the weight of the inorganic siliceous solid substance, a titanium content of 1.5% by weight or less being more preferred. A low titanium content results in improved activity and improved selectivity. In order to give the desired titanium content and desired activity, a multi-stage impregnation process which either goes or does not go through a drying and/or calcining step also may be used.

The catalyst of the present invention may contain a small amount of a catalyst modifier. Examples of the catalyst modifier include alkali metals, such as lithium, sodium, potassium and rubidium, and alkaline earth metals, such as magnesium, calcium, strontium and barium. These modifiers are added in a soluble form to the impregnation solution. In general, suitably 5% by weight (as metals) or less of the catalyst modifier is added to the present catalyst. It is advisable to add about 0.25-1.0% by weight of such a catalyst modifier as sodium, potassium, calcium and magnesium.

The catalyst thus prepared may be used in any desired physical forms, e.g., powders, flakes, spherical particles and pellets.

Oxirane compounds can be produced by reacting an organic hydroperoxide with an olefin in the presence of the catalyst prepared by the method described above.

5 An organic hydroperoxide is a compound having the formula



10 wherein R is a monovalent hydrocarbyl group. The compound reacts with an olefinic compound to form an oxirane compound and a compound R-OH.

R is preferably a group having 3-20 carbon atoms, more preferably a hydrocarbyl group and secondary or tertiary alkyl or aralkyl group, each having 3-10 carbon atoms. Particularly preferred of these groups are tertiary alkyl groups and secondary or tertiary aralkyl groups. Specific examples thereof include the tert-butyl group, tert-pentyl group, cyclopentyl group, 1-phenylethyl-1 group, 2-phenylpropyl-2 group and tetralinyl group formed by removing a hydrogen atom from the aliphatic side chain of a tetralin molecule.

15 Examples of aralkyl hydroperoxide having a hydroperoxy group bonded to a carbon atom present in the alkyl side chain directly bonded to the aromatic ring include ethylbenzene hydroperoxide (1-phenylethyl-1-hydroperoxide) and cumene hydroperoxide (2-phenylpropyl-2-hydroperoxide).

20 When ethylbenzene hydroperoxide is used, the hydroxyl compound obtained is 1-phenylethanol (methyl phenyl carbinol), which can be converted to styrene by dehydration. When cumene hydroperoxide is used, the resulting hydroxyl compound is 2-phenyl-2-propanol (dimethyl phenyl carbinol), which can be converted to α -methylstyrene by dehydration. Both styrene and α -methylstyrene are industrially useful substances.

25 When tert-pentyl hydroperoxide is used, resulting tert-pentyl alcohol is useful as a precursor of methyl tert-pentyl ether, which is an octane number improving agent; and tert-amylene obtained by dehydration of tert-pentyl alcohol is useful as a precursor of isoprene. When t-butyl hydroperoxide is used, resulting t-butyl alcohol is useful as a precursor of methyl t-butyl ether, which is an octane number improving agent.

The organic hydroperoxide used as the starting material may be a dilute or concentrated, purified or unpurified substance.

30 In general, an organic compound having at least one olefinic double bond can be reacted with an organic hydroperoxide. The organic compound may be acyclic, monocyclic, bicyclic or polycyclic and may be monoolefinic, diolefinic or polyolefinic. When the compound has two or more olefinic bonds, the bonds may be either conjugated bonds or non-conjugated bonds. The compound is preferably an olefinic compound having 2-60 carbon atoms. Though the compound may have a substituent, the substituent is preferably a relatively stable group. Examples of such hydrocarbons include ethylene, propylene, butene-1, isobutylene, hexene-1, hexene-3, octene-1, decene-1, styrene and cyclohexene. 35 Examples of the diolefinic hydrocarbons include butadiene and isoprene. The compound may have a substituent, of which an example is a halogen atom. The compound may further have various substituents which comprise an oxygen, sulfur and/or nitrogen atom together with a hydrogen and/or carbon atom. Particularly preferred olefinic compounds are olefinic unsaturated alcohols and halogen-substituted olefinic unsaturated hydrocarbons, examples of which include allyl alcohol, crotyl alcohol and allyl chloride. Particularly preferred are alkenes having 3-40 carbon atoms, which may be substituted with a hydroxyl group or halogen atom.

40 The usefulness of oxirane compounds has been known since long. Many oxirane compounds are useful industrial chemicals, olefin oxides such as ethylene oxide and propylene oxide being particularly important. Propylene oxide can be converted to useful polymeric products by polymerization or copolymerization. Epichlorohydrin, which is also industrially important, can be obtained from allyl chloride. If desired, epichlorohydrin can be converted to glycerol. It is also possible to produce glycerol from an oxirane compound obtained from allyl alcohol.

45 Oxirane compounds can be produced by use of the catalyst composition which is prepared by the method specified above and which is substantially insoluble in the epoxidation reaction mixture and hence can form a heterogeneous system. The above-mentioned catalyst composition used has a very high activity and can convert organic hydroperoxides with a high conversion and has a high selectivity to oxirane compounds. The term "selectivity" herein means the molar ratio of the oxirane compound formed to the organic hydroperoxide converted.

50 In general, an epoxidation reaction can be conducted in a liquid phase using a solvent and/or a diluent. The solvent and diluent are preferably those which are liquid at the temperature and pressure of the reaction and substantially inert to the reactants and the reaction products. The solvent may also be a substance which is already present in the hydroperoxide solution used. For example, when the ethylbenzene hydroperoxide (EBHPO) used is a mixture of EBHPO and ethylbenzene, which is a starting material thereof, the ethylbenzene may be substituted for solvent with no particular addition of solvent. A second solvent also may be used as the diluent. Examples of solvents useful as diluents include aromatic monocyclic compounds (e.g., benzene, toluene, chlorobenzene, bromobenzene and o-dichlorobenzene) and alkanes (e.g., octane, decane and dodecane). It is also possible to use an excessive amount of olefinic reactants as the solvent. Thus, along with the solvent supplied together with an organic hydroperoxide, an excessive amount

Comparative Example 3

An epoxidation reaction was carried out in the same manner as in Example 1 except that 15 mg of TiO₂ (titania) was used as the catalyst. The results of the reaction are shown in Table 1.

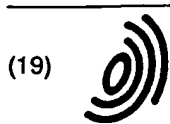
In Table 1, the higher EBHPO conversion means the higher catalyst activity; and the higher selectivity to propylene oxide and the lower selectivity to by-products (which lead to the increase of load in purification) mean the higher selectivity of catalyst. As is apparent from Table 1, the catalysts obtained by a process which, in addition to the steps of prior art processes, further comprises a washing step show increased activity and increased selectivity to intended product and decreased selectivity to by-products (compare Example 1 with Comparative Example 1 and compare Example 2 with Comparative Example 2). With regard to activity, the activity of the present catalyst is improved by 20-30% as judged from the reaction velocity ratio. Further, both of the activity and selectivity increase in the order of Examples 2, 1 and 3, wherein the Ti content decreases in this order.

Table

	Example			Comparative Example		
	1	2	3	1	2	3
Ti content (wt%)	0.75	1.5	0.38	0.75	1.5	60
Activity						
EBHPO conversion (%)	99.93	98.22	99.96	99.62	96.11	7.80
Reaction velocity ratio	2.24	1.24	2.41	1.72	1	0.03
Selectivity (%)						
PO	85.15	83.54	86.89	84.15	83.25	31.60
PNL	0.19	0.26	0.13	0.28	0.35	0.13
BALD	0.14	0.23	0.12	0.17	0.27	0.36
PG	0.33	0.32	0.25	0.36	0.52	1.72
Note: EBHPO: Ethylbenzene hydroperoxide PO : Propylene oxide PNL : Phenol BALD : Benzaldehyde PG : Propylene glycol						

Claims

1. A heterogeneous catalyst used for producing an oxirane compound by reacting an olefinic compound with an organic hydroperoxide which catalyst is substantially insoluble in the reaction mixture, comprises at least one silicon compound, selected from
silica and inorganic silicates, in chemical combination with an oxide or hydroxide of titanium, and is obtainable by a process comprising the steps of:
 - (a) impregnating the silicon compound with a titanium compound in a solvent for impregnation,
 - (b) removing the solvent for impregnation,
 - (c) then washing the remaining composition with a washing solvent and removing the washing solvent, and
 - (d) then calcining the residual composition.
2. A catalyst obtainable by further silylating the catalyst according to claim 1.
3. The catalyst according to claim 1 or 2 wherein the washing solvent is an alcohol.
4. The catalyst according to any of claims 1 to 3 which is obtained by conducting the washing at from 10 to 60°C.



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